# ON THE FREEZING OF GEL.

By Kyoji KINOSHITA.

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The structure of gels which are formed by setting of the hydrophilic colloids such as gelatine, agar or starch etc. have been studied by numerous authors, and several opinions[1] were given on this subject. Formerly it was considered to be a homogeneous or one phase system. But now, generally, two phases theory is adopted for, in some cases, even optical resolution into two phases are possible. The two phases theory are subdivided into two, namely liquid-liquid system and solid-liquid system. Whichever we may take, it will be interesting to study the nature of water in the gel. The present experiment have been undertaken to study this problem by freezing of gels.

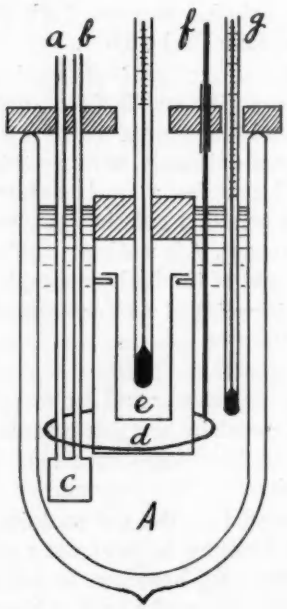


Fig. 1.

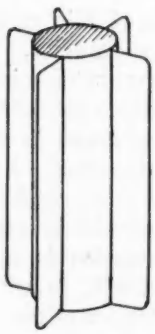

Fig. 2.

(1) For example, Hardy, *Proc. Roy. Soc.*, A, **66** (1900), 95; Lloyd, *Biochem. J.*, **14** (1920), 147, 584; Bogue, *J. Am. Chem. Soc.*, **44** (1922), 1343.

Moran[1] and Hardy[2] observed the microstructure of gels and the volume change by freezing. Most interesting result drawn from their experiments is an equilibrium relation between gel and ice.

According to Moran, when 12–40% gelatine gel was cooled at -3°C a part of water separated from the gel and solidified into ice and covered the unfrozen gel. Taking off the shell of ice the internal gel has a constant concentration depending on the freezing temperature. For example, the gel frozen at -3°C. always has 54.3% internal gel concentration and at -19°C. internal gel concentration reached 65.2%. He also reported that the frozen gel reabsorbs water if it was warmed and the gel comes back to its initial concentration. From these and other observations he concluded that there are two kinds of water in a gel, namely the water combined with gelatine particles and the water contained in a capillary formed by the aggromeration of these particles. In the case of gelatine gel 30% of water is said to combine with gelatine particles.

**Experimental.** Commercial food gelatine was used all through the experiments, ash content of which was found to be 0.5%.

Cooling apparatus used for the freezing of gel is shown in Fig. 1. *A* is a Dewar's vessel of about 1 litre capacity and is filled with petroleum ether. The liquid air was dropped into the copper vessel *c* through the tube *a*, which then vaporizes and escapes through another tube *b*. *d* is a vessel made of thin copper plate and contains a small copper vessel *e* of about 20 c.c. capacity. The vessel *e* contains gelatine gel, and a Beckmann's thermometer is inserted into the gel. *f* is a stirrer, and *g* a pentane normal thermometer for the measurement of the bath temperature.

Gelatine, stored in a desiccator, is weighed and some amount of distilled water is added. After the swelling of gelatine was completed it is heated on a water bath for a while to obtain a homogeneous solution. A part of the solution is transferred into the vessel *e* and let to set into a gel. Remaining portion is taken into a porcelain crucible and is heated to dryness at 100°C. in an air bath untill the weight constant is attained. The concentration of the gel is determined by this manner.

Beckmann's thermometer is inserted into the gel contained in *e* and the reading is taken every 30 seconds in order to construct a cooling curve of the gel. The Beckmann's thermometer, however, is not sufficiently sensitive to the small change of temperature, so the bulb of thermometer is dipped into mercury contained in a copper cylinder to which some copper

(1) Moran, *Proc. Roy. Soc.*, A, **112** (1926), 30.
(2) Hardy, *Kolloid-Z.*, **46** (1928), 270.

wings are attached (Fig. 2). This small cylinder with wings is inserted into gel and the temperature of gel is measured indirectly. Gelatine gel increases its volume when it is frozen, and we have experienced that, if we insert a thermometer directly into a gel the mercury bulb is subjected to a high pressure, so that not only the thermometer indicates an incorrect reading but also it is liable to be broken by the pressure. Using the above described small cylinder we can get rid of these inconveniences.

**Results of Measurement.** Some of the cooling curves of gels, which we have obtained in the various concentrations of gelatine (from 5% to 60%) are shown in Fig. 3. As seen from the figure, the phenomena of supercooling is appeared very markedly. This may explain as a result of protective actions of gelatine on the formation of ice nucleus and on the growing of ice crystals.

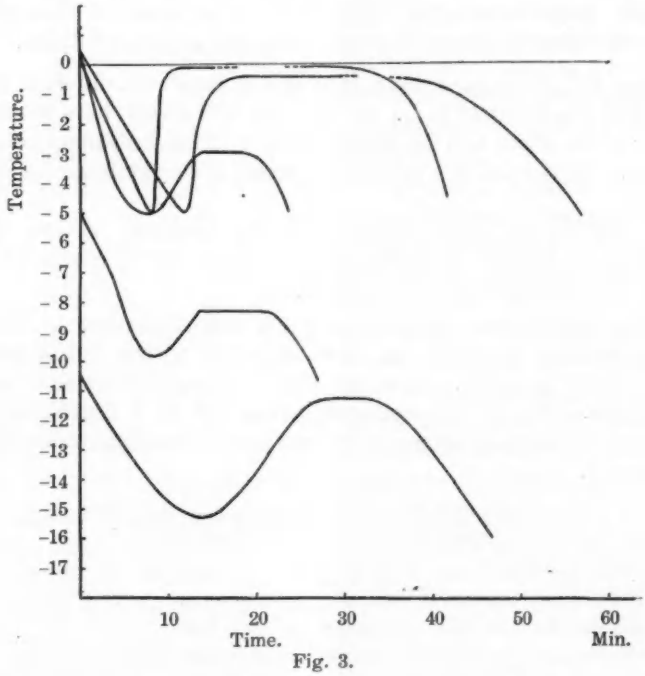


Fig. 3.

It is noteworthy, moreover, that the structure of the frozen gel thus produced differ from each other according to their concentrations. Namely, in the case of gel below 15% frozen in a cylindrical vessel, the concentric

thin layers of ice and gel are seen. The layers come alternately and the thickness of which are about 0.5 mm. Of these alternating shells the first shell is always of ice. When it is left to thaw, then again it absorbs water from ice into the layer of gel. However, a little quantity of water can be squeezed out by pressing, immediately after it thawed. Therefore, it seems that the melted ice is reabsobed by the swelling of the gel if we do not press it.

Formation of these shells can be explained in the following manner. At first water which can be separated by cooling comes out of gel (dehydration of gel is caused) and forms shell of ice but the effect of this dehydration of gel does not go very deep into the gel owing to its poor heat conductivity. Thus the thin gel layer under the shell of ice is concentrated by dehydration, and this layer of gel does not freeze by cooling, for its freezing point is lowered by dehydration so that it remains unchanged. Then the cooling effect goes deeper and again a layer of ice is formed. This process is repeated and thus the alternate shells of ice and gel are produced.

Frozen gel of stronger than 20% shows somewhat different structure from that of weaker than 15%. In this case it is a very hard mass of pale brownish white colour and the separation of water as ice cannot be observed with eyes. By the use of a microscope small ice crystals can be seen here and there.

The gelatine gel increases its volume by freezing. Moran measured the change of volume by using a dilatometer, but I could not do any quantitative measurement on this point.

Similar cooling curve can be seen in a case of starch gel. The frozen starch gel is white in colour, and when it is left on the funnel to thaw it secredes water in drops. Agar gel slso becomes whitish and are found many cracks. The frozen agar gel, when left on a funnel to thaw, it separates water drop by drop, and we can press out considerable amount of water from it.

| Conc. of gelatine gel by weight %. | Freezing temeprature °C. |
|---|---|
| 5 | – 0.10 |
| 10 | – 0.42 |
| 15 | – 2.96 |
| 20 | – 5.66 |
| 25 | – 8.33 |
| 30 | – 9.74 |
| 40 | –11.25 |
| 60 | –12.65 |

It is almost a doubtless fact that the hydrophilic colloids are in hydrated states. Many authors have reported the investigations on the degree of hydration. Moran determined the quantity of water separated from a frozen gel as ice, and concluded that the degree of hydration in the case of gelatine is about 30%.

The freezing temperatures of various gels obtained by the present experiment are shown in the table above.

Plotting these values on a temperature concentration diagram we obtain a curve of inverse S type (Fig. 4). In the case of 5% and 10% gel we find that its freezing temperature is nearly equal to, or little lower than that of pure water. The form of cooling curve obtained in this case is similar to the curve which can be obtained when the pure ice is separated from the solution. In the case of 15–30% gel freezing temperature falls suddenly, and in the 40% up to 60% gel freezing temperature curve becomes asymptotical to the axis of concentration.

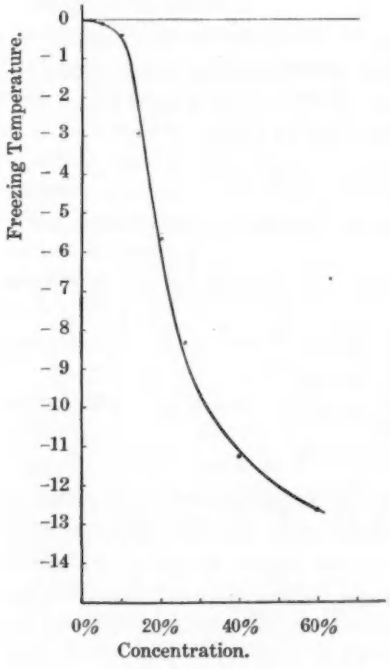

Fig. 4.

Now let us assume that the gelatine particle can take any degree of hydration according to its concentration. These hydrated water molecules have their own strength of hydration, some of them may cling to the particle very strongly and others may be very weakly attach to the particle, just as we can see in the case of ion-atmosphere around the ion of strong electrolyte. Weakly attached water must be separated when gel is subjected to dehydration, and the constitution of dehydrated gel must depend on the process and intensity of dehydration. In the above experiments 5–15% gel has a weakly combined water which can be separated out by freezing, so that there remains the mixture of gel and ice. In the gel more concentrated than 15% there is no water which can be separated by freezing, and hence it freezes in a hydrated state, and is turned into a pale brownish white mass. In the case of 40–60% gel, the freezing point curve

runs asymptotically to the axis of concentration. From this fact it is probable that some water must be combined in gel rather strong, in the form of chemical compound or of solid solution. By these assumptions we can explain the above described formation of alternating shell of ice and gel.

In conclusion, I should like to express my hearty thanks to Prof. J. Sameshima for his kind guidance throughout my experiments.

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## ACTION OF REDUCED NICKEL AND HYDROGEN ON AROMATIC HYDROCARBONS UNDER HIGH PRESSURE AND TEMPERATURE.

By Toru OGAWA and Toshio YOKOTA.

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The reduction of benzene was assumed to proceed by the following steps:

$$C_6H_6 + H_2 = C_6H_8 + 0.8 \text{ cal.}$$
$$C_6H_8 + H_2 = C_6H_{10} + 25 \text{ cal.}$$
$$C_6H_{10} + H_2 = C_6H_{12} + 27.8 \text{ cal.}$$
$$C_6H_{12} + H_2 = C_6H_{14} + 11 \text{ cal.}$$

which were investigated comprehensively by Stohmann[1] in the series of his thermochemical studies of organic compounds, and he concluded that the jump in heat-toning between the first and second terms of the series compared with the two following, as well as between the third and fourth, indicates a fundamental difference of structure between benzene and its di- and tetra-hydrobenzenes, and also between tetrahydro- and hexahydrobenzenes, viz., that the benzene molecule is in the most stable state by packing together by the bonds and the combination by them in di- and tetra-hydrocompounds more loosely, reaching again a high degree of stability in hexahydrobenzene, and such observation led him to reject the Kekulé formula for benzene.

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(1) *J. prakt. Chem.*, **48** (1893), 447; **49** (1894), 260.

The structural formula for naphthalene proposed by Graebe was also rejected by Bamberger[1], and lately by Willstätter[2] from their studies of its reduction.

According to Professor Sabatier[3] benzene begins the catalytic hydrogenation to cyclohexane in presence of reduced nickel at 70° and proceeds with increased velocity as the temperature is increased to about 300°, and above this temperature there is no formation of cyclohexane, but the conversion of the latter into benzene and decomposition into methane and carbon have started. Under similar conditions naphthalene yields tetralin and decalin which decompose at high temperature into methane and benzene homologues.

When benzene and naphthalene treated in presence of nickel oxide at high temperature and under pressure, the experimental results[4] are on the whole very similar to those obtained by Sabatier's method.

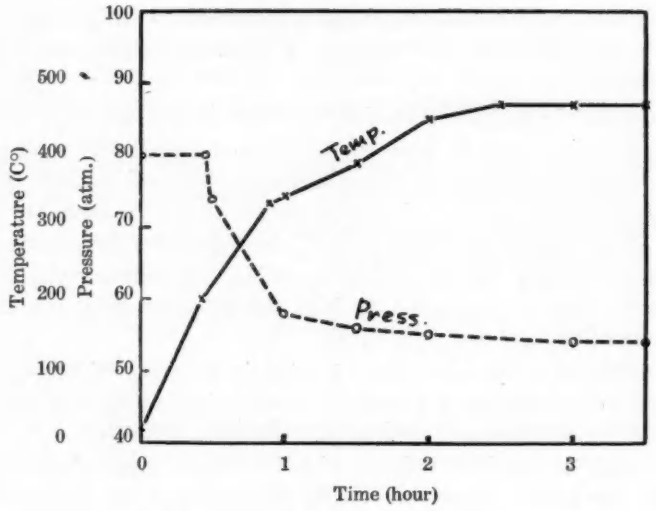
The catalytic action of reduced nickel at high temperature and under pressure, apart from these theoretical considerations on the structure of aromatic hydrocarbons, would afford an idea for the cracking process in which permanent gas and volatile fuels for internal combustion engines are prepared from heavy hydrocarbons, and the formation of these compounds is regarded generally as depending on the temperature and pressure at which the process is carried out, with or without catalyst and hydrogen, and the present investigation was so carried out.

In the experiment, 100 gr. of pure benzene, b.p. 80°–80.5° (761 mm.), $n_D^{25}=1.498$, were introduced in an autoclave of 2 litres capacity, with 5 gr. of reduced nickel and hydrogen, and heated at 470° for 1 hour, under pressure of 80 atmospheres at 0°, after cooling the apparatus, the depression of pressure of hydrogen was 35 atm. at 0°, which corresponds to 2.7 mol %. (Fig. 1.) The gas in the autoclave was analysed with the following results:

| $CO_2$ | CO | $C_nH_{2n}$ | $C_nH_{2n+2}$ | $H_2$ | n |
|---|---|---|---|---|---|
| 0.1 | — | — | 1.4 | 98.5 | 1.2 |

The liquid reaction product was 92% in yield for theory, and on being fractionated:

(1) *Ann.*, **257** (1890), 47.
(2) *Ber.*, **45** (1912), 1478.
(3) "La catalyse en chimie organique," (1920), p. 171, 221.
(4) W. N. Ipatiew "Aluminiumoxyd als Katalysator in der organischen Chemie," (1929), 78.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Pressure (atm.)
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Temp.
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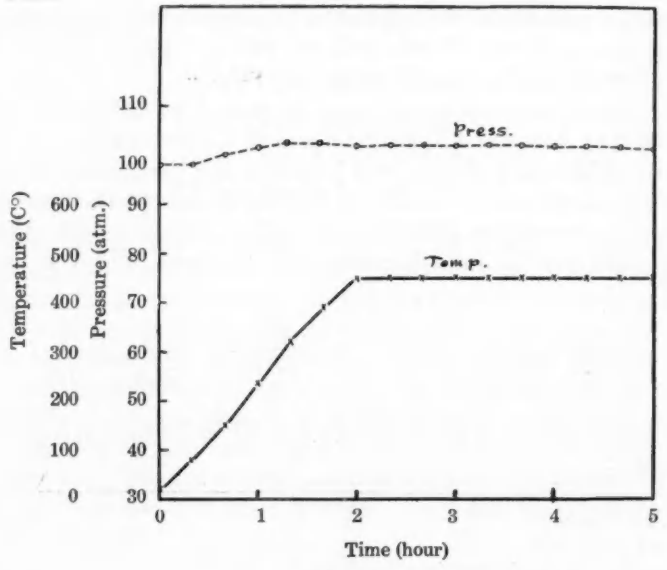
Fig. 1.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100
40
0
30
0
1
2
3
4
5

Fig. 2.

| | Fraction | Yield | $n_D^{25}$ | $d_4^{25}$ |
|---|---|---|---|---|
| 1 | 77°–79° | 55% | 1.433 | 0.7843 |
| 2 | 79°–80.7° | 30% | 1.433 | 0.7806 |

The two fractions showing no reaction with bromine, were treated with a mixture of nitric and sulphuric acids, and show b.p. 80°–82°, $n_D^{25}=1.423$, $d_4^{25}=0.777$ which agree with the constants for cyclohexane.

When 166 gr. of pure cyclohexane heated in presence of hydrogen and 20 gr. reduced nickel in the autoclave at 450° for 3 hours under 100 atmospheric pressures at 0°, no appreciable change on pressure was noticed as indicated in Fig. 2, and the liquid substance in the autoclave boils from 80° to 85°, and thus cyclohexane is confirmed to be a stable compound under the above conditions, and the same is also noticed of benzene treated with hydrogen at 460° for 1 hour, and 100 atmospheric pressures at 0°.

While, benzene heated for 5 hours with hydrogen in presence of reduced nickel at 500°, under pressure of 100 atmospheres at 0°, undergoes the hydrogenation which follows with decomposition of the hydrogenated compound into methane on the one hand, and on the other into aromatic hydrocarbons. (Fig. 3).

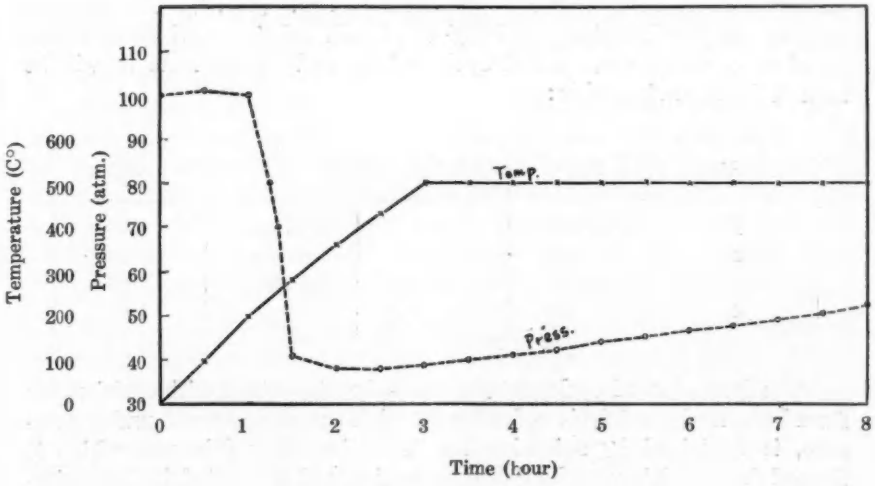


Fig. 3.

The reaction products are 28% gas, 41% liquid hydrocarbons and 14% coke. The gas was composed of 94.5% methane and 5.5% hydrogen. The liquid product was fractionated as follows:

| Fraction | B.p. | % | $n_D^{25}$ | $d_4^{25}$ |
|---|---|---|---|---|
| 1 | 48°– 65° | 0.6 | 1.413 | — |
| 2 | 65°– 75° | 1.4 | 1.446 | 0.789 |
| 3 | 75°– 85° | 6.5 | 1.492 | 0.859 |
| 4 | 85°–120° | 5.5 | 1.494 | 0.866 |
| 5 | 120°–180° | 2.3 | 1.502 | 0.875 |
| 6 | 180°–250° | 2.6 | 1.551 | 0.942 |
| 7 | 250°–300° | 2.3 | 1.603 | 1.012 |
| 8 | 300°–320° | 1.5 | 1.651 | 1.07 |
| 9 | Residue | 3.6 | — | — |

These results indicate that the fractions are composed of aromatic hydrocarbons, and benzene and toluene occur in fractions 3 and 4.

When benzene was first heated with hydrogen in presence of the catalyst under 200° and 100 atmospheric pressures at 0° for 2 hours, 3.9 mol % of hydrogen were absorbed, and the product was again heated at 500° for 3 hours with a new supply of hydrogen of 78 atmospheric pressures, and a depression of 17 atm. was noticed. (Fig. 4.) The reaction product was 5.4% methane and 95% of a liquid substance which was composed of cyclopentane, methyl cyclopentane and cyclohexane as will be seen in the following table:

| Fraction | B.p. | Yield | $d_4^{25}$ | $n_D^{25}$ |
|---|---|---|---|---|
| 1 | 48°–65° | 2.9 | 0.744 | 1.409 |
| 2 | 65°–75° | 28.7 | 0.753 | 1.415 |
| 3 | 75°–85° | 31.7 | 0.772 | 1.424 |
| 4 | 85°–90° | 0.4 | — | 1.423 |

The formation of cyclopentane, methyl cyclopentane with cyclohexane from benzene by catalytic reduction at high temperature and under pressure, is explained by assuming the formation of cyclohexene which is formed from cyclohexane by dehydrogenation and converted by isomerisation into methyl cyclopentane. The latter phase of the reactions has al-

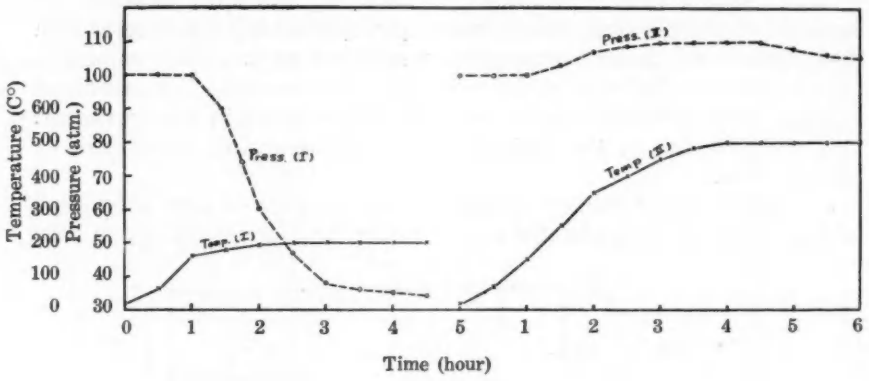


Fig. 4.

ready been noticed by Dr. H. Inoue[1] in his study on the catalytic action of Japanese acid earth on cyclohexanol and its drivatives, where cyclohexanol by passing on the catalyst heated at 200° was converted into cyclohexene, while at a high temperature, such as 330°, methyl cyclopentane occurred in the reaction product, which was actually derived from cyclohexene by the contact action of the catalyst at high temperature.

Such a view for the conversion of cyclohexane into cyclohexene was also accepted by D. T. Jones[2] in the transformation of cyclohexane, heated to 500° in contact with porous porcelain, into hydrogen, ethane, benzene and some olefine hydrocarbons.

According to Ipatiew cyclohexane at high temperatures such as 600° appears to be more stable than n-hexane, and the isomerization of cyclohexane into methyl cyclopentane takes place under high pressure and in presence of alumina, but with ordinary pressure, even at 760°, there is no such isomerization.[3] These facts are in harmony with the writers' case that cyclohexane and methyl cyclopentane occur in the product from benzene by catalytic reduction, but there is no formation of n-hexane.

**Naphthalene.** Although naphthalene[4] itself gives no benzene on pyrolysis, dihydronaphthalene, tetralin and decalin pyrolyse at about 400° in forming hydrogen and naphthalene as chief products with some methane,

(1) This Bulletin, **1** (1926), 219.
(2) *J. Chem. Soc.*, **107** (1915), 1582.
(3) *Ber.*, **37** (1904), 2961; **44** (1911), 2987.
(4) Egloff, *J. Soc. Chem. Ind.*, **35** (1916), 920.

ethane, benzene and unsaturated hydrocarbons.[1] In order to study the behavior of these hydrocarbons toward the catalyst and hydrogen at high temperature and under pressure, pure naphthalene b.p. 215°; m.p. 80°, was heated with hydrogen at 460°–500° under 80 atmospheric pressures at 0°, and no appreciable reaction was noticed to occur in the treatment. A similar situation is also noticeable even in presence of ferric oxide or copper oxide.

When, however, 100 gr. of naphalene in presence of 5 gr. of reduced nickel and hydrogen are heated at 470° and under 80 atmospheric pressures

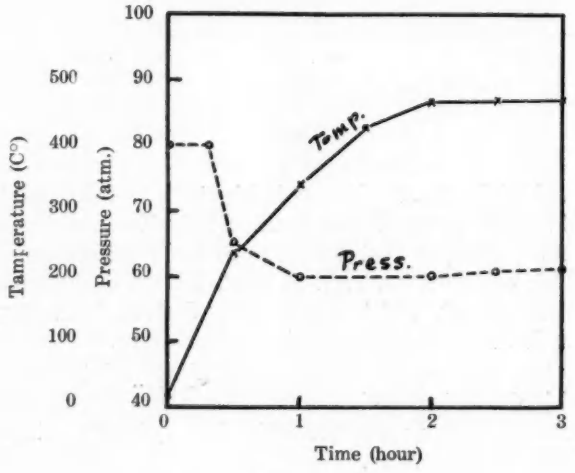


Fig. 5.

at 0° (Fig. 5.) yield 5% methane and 91% of a liquid substance which seems by fractional distillation to be composed of benzene homologue and tetralin as indicated in the table:

| | Fraction | Yield | $d_4^{25}$ | $n_D^{25}$ | Remark |
|---|---|---|---|---|---|
| 1 | 100°–150° | 7% | 0.825 | 1.487 | Benzene homologue |
| 2 | 150°–180° | 8 ,, | 0.895 | 1.498 | |
| 3 | 180°–190° | 18 ,, | 0.901 | 1.502 | Tetralin |
| 4 | 190°–200° | 26 ,, | 0.935 | 1.521 | |
| 5 | 200°–210° | 26 ,, | 0.962 | 1.542 | |
| 6 | Residue | 2 ,, | — | — | |

(1) Jones, loc. cit.

**Tetralin.** When 100 gr. of tetralin, b.p. 206° (760 mm.) treated in presence of hydrogen and the catalyst under the same conditions described in the case of naphthalene (Fig. 6.), 5.6% methane and 92% of a liquid sub-

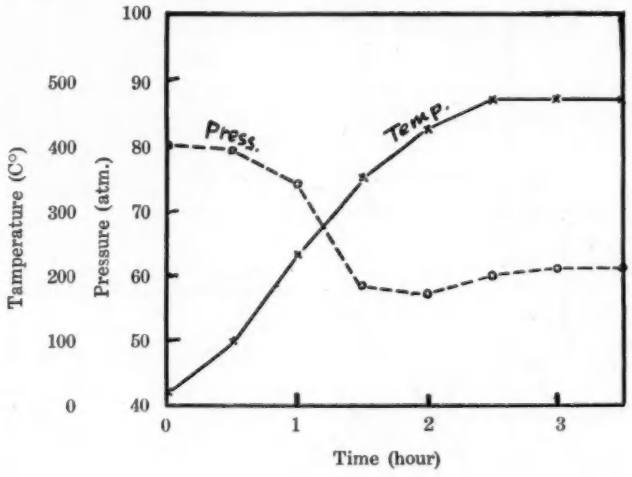


Fig. 6.

stance are formed and the latter is composed of benzene homologue and decalin.

| | Fraction | Yield | $d_4^{25}$ | $n_D^{25}$ | Remark |
|---|---|---|---|---|---|
| 1 | 85°–180° | 28 % | 0.845 | 1.454 | Benzene homologue |
| 2 | 180°–185° | 39 „ | 0.874 | 1.473 | |
| 3 | 185°–188° | 18 „ | 0.879 | 1.477 | Mostly decalin |
| 4 | 188°–191° | 5 „ | 0.889 | 1.483 | |
| 5 | Residue | 2 „ | — | — | |

**Decalin.** 200 gr. of pure decalin, b.p. 188° (760 mm.) heated with 20 gr. reduced nickel and hydrogen to 450° under 100 atmospheric pressures at 0° for 3 hours (Fig. 7), 3% methane and 97% of a liquid substance of the following compositions are formed.

When decalin is heated in presence of reduced nickel and hydrogen at 450° under 100 atmospheric pressures at 0°, only one part of the com-

pound was decomposed into cyclohexane derivatives, while tetralin and naphthalene under similar conditions tend to be transformed into benzene homologues and decalin and benzene homologues and tetralin respectively.

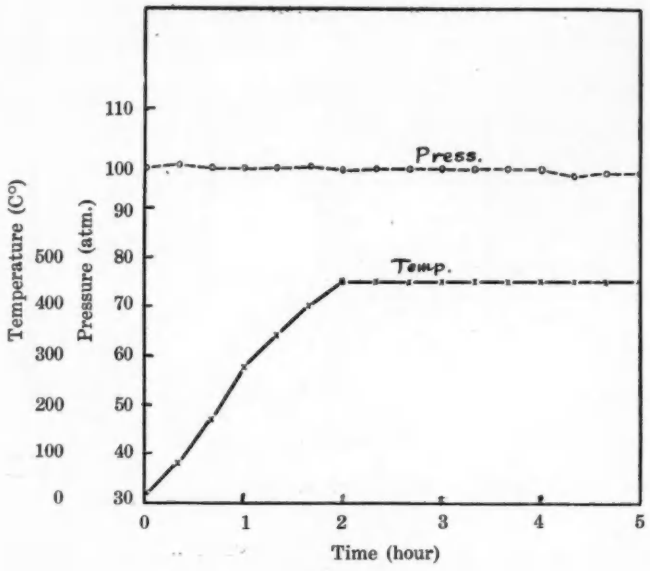


Fig. 7.

| | Fraction | Yield | $d_4^{15}$ | $n_D^{20}$ | Remark |
|---|---|---|---|---|---|
| 1 | 29°– 90° | 3 % | 0.777 | — | Cyclohexane and its homologue |
| 2 | 90°–130° | 6 ,, | 0.785 | 1.437 | |
| 3 | 130°–150° | 7 ,, | 0.826 | 1.451 | |
| 4 | 150°–188° | 81 ,, | 0.872 | 1.469 | Mostly decalin |
| 5 | 188°–192° | 2 ,, | 0.889 | 1.476 | |

The fact that tetralin decomposes into benzene homologues with fruitful yield is in favour of the view that the naphthalene molecule is in a more stable state than tetralin. The stability of hydronaphthalene again reaches a maximum in decahydronaphthalene. The relation in chemical behavior among naphthalene and its reduced compounds by the process of cracking

in presence of reduced nickel and hydrogen is on the whole very similar to that among benzene and its hydrogenated compounds.

In conclusion, the writers wish to express their sincere thanks to Vice-Admiral S. Kishimoto, Director of the Imperial Naval Fuel Depot, who gave them permission to publish this paper; to Engineer-Captain Viscount M. Kawase, Chief of the Scientific Research and Experimental Branch, for their kindness in enabling them to take part in this work; and also to Professor S. Komatsu of the Kyoto Imperial University, whose advice and encouragement have been invaluable.

June 1930.

Naval Fuel Depot, Imperial Japanese Navy,
Tokuyama.

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## X-RAY INVESTIGATIONS ON COPPER-ARSENIC ALLOYS.

By Nobuyuki KATOH.

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**Earlier Investigations.** According to the thermal and microscopic investigations of Hiorns[1] there should exist no less than three intermediate phases in the copper-arsenic system within the range 0–44% As, corresponding to the formulas $Cu_3As$, $Cu_5As_2$ and $Cu_2As$. Friedrich[2] using the same methods of investigation, claims to have found $Cu_3As$ and $Cu_5As_2$, but he did not confirm the existence of $Cu_2As$.

The electrical properties of these alloys were first studied by Matthiessen and Holzmann.[3] Friedrich[4] observed an abrupt change of direction in the conductivity curve at the limit of the saturation, of arsenic in the copper phase. Puschin and Dischler[5] measured the conductivity of a series of alloys containing up to 43% As. This investigation have only confirmed the existence of one intermediate phase, namely $Cu_3As$.

By passing arsenic vapour over hot copper Koenig[6] succeeded in producing macroscopic crystals of $Cu_3As$ which have been subjected to cryst-

(1) A. Hiorns, "Electro-chemist and Metal," (1904).
(2) K. Friedrich, *Metallurgie*, **5** (1908), 529.
(3) A. Matthiessen and Holzmann, see *Metallurgie*, **5** (1908), 529.
(4) K. Friedrich, ibid.
(5) N. A. Puschin and E. Dischler, *Z. anorg. Chem.*, **80** (1913), 65.
(6) G. A. Koenig, *Z. Kryst.*, **38** (1903), 529.

allographic measurements. According to Stevanoic[1] they crystallize in orthorhomic system with axial ratios 0.5771:1:1.0206, while Wright[2] describes the symmetry as hexagonal with an axial ratio 1:1.539.

Quite recently Ramsdell[3] found that crystals of $Cu_3As$ produced by Koenig's method and material produced by fusion give the same X-ray pattern, a result which has been confirmed by the present author. Although the crystals are quite well developed, the powder photograms show that their composition is not uniform. Ramsdell made no attempt to determine the structure.

By melting the theoretical quantities of the components in an evacuated quartz tube, Machatschki[4] prepared alloys of the compositions $Cu_3As$ and $Cu_5As_2$, and subjected them to an X-ray investigation. All interferences of $Cu_3As$ were accounted for by a quadratic form of the hexagonal type, and the lattice dimensions were found to be the following:

$$a=7.200\text{Å}, \qquad c=7.478\text{Å}.$$

The axial ratio is $c:a=1.039$.

Machatschki also made a goniometoric determination of the axial ratio of crystals obtained by Koenig's method, The following table shows the result obtained by him compared with those which he has calculated from the data of Stevanoic and of Wright.[5]

| | c:a |
|---|---|
| Machatschki . . . . . | 1.023 |
| Stevanoic . . . . . | 1.0206 |
| Wright . . . . . | 1.0259 |

The alloy with the composition $Cu_5As_2$ was found by Machatschki to be inhomogeneous but to consist mainly of a phase with the same structure as $Cu_3As$ but with slightly different lattice dimensions.

**Preparation of Samples and their Chemical Analysis.** The alloys with less than 30% As were prepared in a high frequency induction furnace in nitrogen atmosphere,[6] 20 grams of electrolytic copper were first melted in a magnesia crucible. The arsenic (Kahlbaum) was then dropped

(1) S. Stevanoic, *Z. Kryst.*, **37** (1903), 246.
(2) F. E. Wrignt, *Z. Kryst.*, **38** (1903), 509.
(3) L. S. Ramsdell, *The American Mineralogist*, **14** (1929), 188.
(4) F. Machatschki, *Neues Jahrbuch für Mineral.*, **59**, Bl. Bd. (1929), 137; *Centralblatt für Mineralogie*, A, (1930), 13–19.
(5) Loc. cit.
(6) G. Hägg, *Nova Acta Regiæ Soc. Scient. Ups.*, Ser. IV, 7, No. 1 (1929).

into the melt. The alloys with higher content of arsenic were prepared by melting copper and arsenic together in an evacuated quartz tube, as described by Thomassen.[1] In order to obtain a uniform product, the tube was turned after fusion, allowing the melt to flow down along the wall of the tube. Samples of 6 to 7 grams were prepared in this way.

The composition of the samples could be estimated by weighing the product obtained and assuming that no copper was lost during the melting process.[2] The content of copper was, however, also determined analytically by one of the following methods.

All samples were dissolved in warm nitric acid and evaporated with sulphuric acid. When the arsenic content was low, a copper sulphate solution free from arsenic was obtained by evaporation with hydro-fluoric acid. Copper was then determined electrolytically in the presence of nitric acid.[3] The samples with higher content of arsenic were treated according to a method described by Jannasch and Biedermann.[4] The sulphate solution was made strongly alkaline and the copper was reduced by hydrazine sulphate. The copper was then dissolved in acid and determined iodometrically.

**X-ray Analysis.** The X-ray tube used was of the Hadding-Siegbahn type and was run at 45 kv. and 10 ma. Three cameras of the focussing type[5] covering together the whole diffraction range, were used. The time of exposure varied from 5 to 8 hours. The cameras were constructed by G. Phragmen and were calibrated with sodium chloride. The K-radiation of chromium was used throughout the work.

**The $\alpha$ Phase.** According to Friedrich,[6] copper dissolves about 4% As at room temperature. The dimensions of the face-centred cubic copper phase ($\alpha$) increase with the arsenic content. While the edge of the elementary cube is for pure copper 3.608Å, it was found to be 3.629Å for an alloy with 2.0% As. At the limit of solubility at room temperature the edge was found to be 3.640Å.

**The $\beta$ Phase.** Friedrich found the $\beta$ phase to have a homogeneity range extending from 28.6 to 29.6 % As. This was confirmed by the present author. As already mentioned, Machatschki succeeded in finding the ele-

(1) L. Thomassen, *Z. physik. Chem.*, **135** (1928), 385.
(2) Puschin, loc. cit.
(3) A. Classen, "Quantitative Analyse durch Elektrolyse," (1927).
(4) P. Jannasch and K. Biedermann, *Ber.*, **33** (1900), 631.
(5) H. Bohlin, *Ann. der Physik*, **61** (1920), 422; A. Westgren and G. Phragmen, *Phil. Mag.*, **50** (1925), 318.
(6) Loc. cit.

mentary dimensions of this phase. Before Machatschki's work was published, the present author had also found the quadratic form. The following dimensions were determined by the author.

| | a | c | c : a |
|---|---|---|---|
| Cu-limit of homogeneity range | 7.121 Å | 7.293 Å | 1.024 |
| 29.1 % As | 7.118 Å | 7.279 Å | 1.023 |
| As-limit of homogeneity range | 7.095 Å | 7.267 A | 1.024 |

The density of $Cu_3As$ was determined by several authors as follows:

| | |
|---|---|
| Stevanoic . . . . . | 7.02–8.10 |
| Weisbach . . . . . | 7.0–7.5 |
| Machatschki . . . . . | 7.88 |
| Calculated from Koeing . . . . | 7.94 |

The most probable number of molecules in the unit cell is 6, which according to the X-ray data of the author would give the theoretical density 8.22.

Table 1 gives the X-ray data of an alloy within $\alpha$–$\beta$ two phase range. Table 2 shows the data of a slowly cooled alloy with 30.9% As, only faint lines appear besides those belonging to the $\beta$ phase. When the same specimen was quenched from 630°C., however, a number of new lines appeared (Table 3). This might also expected from Friedrich's diagram. The lines of the $\beta$ phase occupy exactly the same positions in both photograms, which shows that the limit of the homogeneity range is not appreciably influenced by the temperature.

Alloys with higher content of arsenic will be subjected to continued investigations. An alloy with the composition $Cu_5As_2$ was tempered at 700°C. for 7 days and quenched from 670°C. The photogram was not homogeneous but showed lines belonging to the $\beta$ phase. A quenched alloy containing 38.7% As contains no more $\beta$ phase. It was found to consist of primary crystals in an eutectic. The author confirmed Friedrich's observation that these primary crystals slowly decompose into two new phases.

Table 1.

Powder Photogram of a Cu-As Alloy with 19.6 % As.

Chromium-K-radiation.

| Intensity | $\sin^2\vartheta/2_{obs.}$ | Radiation | h k l | $\sin^2\vartheta/2$ | h k l | $\frac{\sin^2\vartheta/2}{\Sigma h^2}$ |
|---|---|---|---|---|---|---|
| w | 0.0995 | $\alpha$ | 002 | 0.0982 | | |
| w | 0.1042 | $\alpha$ | 110 | 0.1029 | | |
| w | 0.1289 | $\alpha$ | 111 | 0.1275 | | |
| w | 0.2020 | $\alpha$ | 112 | 0.2011 | | |
| m | 0.2361 | $\alpha$ | 202 | 0.2354 | | |
| St | 0.2453 | $\beta$ | | | 111 | .0818 |
| m | 0.2555 | $\beta$ | 300 | 0.2558 | | |
| w | 0.2642 | $\alpha$ | 211 | 0.2647 | | |
| w | 0.2686 | $\beta$ | 113 | 0.2683 | | |
| v. St | 0.2958 | $\alpha$ | | | 111 | .0986 |
| St | 0.3088 | $\alpha$ | 300 | 0.3088 | | |
| St | 0.3238 | $\alpha$ | 113 | 0.3239 | | |
| v.w | 0.3380 | $\alpha$ | 212 | 0.3384 | | |
| v.w | 0.3465 | | | | | |
| St | 0.3946 | $\alpha$ | | | 200 | .0987 |
| v.w | 0.4070 | $\alpha$ | 302 | 0.4070 | | |
| m | 0.6323 | $\alpha$ | 223,214 | 0.6328, 0.6331 | | |
| v.w | 0.6540 | $\beta$ | | | 200 | .0818 |
| St | 0.7889 | $\alpha_1$ | | | 220 | .09861 |
| m | 0.7919 | $\alpha_2$ | | | 220 | .09899 |
| w | 0.9000 | $\beta$ | | | 311 | |
| w | 0.9254 | $\alpha_1$ | 330 | 0.9254 | | |
| w | 0.9285 | $\alpha_2$ | 330 | 0.9285 | | |
| w | 0.9408 | $\alpha_1$ | 404 | 0.9408 | | |
| w | 0.9436 | $\alpha_2$ | 404 | 0.9442 | | |

## Table 2.

Powder Photogram of a Slowly Cooled Cu-As Alloy Containing 30.86 % As. Chromiun K-radiation.

| Intensity | $\sin^2\theta/2_{obs.}$ | h k l | $\sin^2\theta/2_{calc.}$ |
|---|---|---|---|
| m | 0.0987 | (002) | 0.0998 |
| w | 0.1035 | 110 | 0.1037 |
| w | 0.1296 | (111) | 0.1284 |
| w | 0.1716 | | |
| w | 0.1968 | β 202 | 0.1966 |
| w | 0.2032 | (112) | 0.2025 |
| St | 0.2378 | 202 | 0.2371 |
| m | 0.2569 | 300 | 0.2579 |
| w | 0.2656 | 211 | 0.2667 |
| v. St | 0.3106 | 300 | 0.3111 |
| v. w | 0.3176 | | |
| v. St | 0.3253 | 113 | 0.3261 |
| m | 0.3399 | 212 | 0.3408 |
| m | 0.4089 | (302) | 0.4099 |
| w | 0.4290 | 104 | 0.4299 |
| v. w | 0.4385 | (221) | 0.4395 |
| v. w | 0.4735 | 311 | 0.4741 |
| v. w | 0.4990 | (114) | 0.4991 |
| w | 0.5279 | β 214, β 223 | 0.5284, 0.5284 |
| St | 0.6371 | $\alpha_1$ 214, $\alpha_1$ 223 | 0.6372, 0.6374 |
| w | 0.6386 | $\alpha_2$ 214, $\alpha_2$ 223 | 0.6396, 0.6394 |
| v. w | 0.6822 | 321 | 0.6815 |
| w | 0.7506 | (411) | 0.7508 |
| m | 0.7557 | 205, 322 | $\alpha_1$ 0.7560, $\alpha_1$ 0.7556 |
| w | 0.7583 | 205, 322 | $\alpha_2$ 0.7587, $\alpha_2$ 0.7583 |
| m | 0.8449 | 314 | 0.8448 |
| w | 0.8481 | 314 | 0.8481 |
| v. w | 0.8594 | 215 | 0.8598 |
| m | 0.8897 | 501, 006 | $\alpha_1$ 0.8889, $\alpha_1$ 0.8896 |
| w | 0.8938 | 501, 006 | $\alpha_2$ 0.8921, $\alpha_2$ 0.8928 |
| St | 0.9334 | 330 | $\alpha_1$ 0.9334 |
| w | 0.9363 | 330 | $\alpha_2$ 0.9366 |
| St | 0.9485 | 404, 413 | $\alpha_1$ 0.9485, $\alpha_1$ 0.9484 |
| m | 0.9522 | 404, 413 | $\alpha_2$ 0.9518, $\alpha_2$ 0.9517 |
| w | 0.9635 | 502 | 0.9631 |

## Table 3.

**Powder Photogram of an Cu-As Alloy with 30.86 % As Quenched from 630°C. Chromium K-radiation.**

| Intensity | $\sin^2 \vartheta/2_{obs.}$ | Radiation | h k l | $\sin^2 \vartheta/2_{calc.}$ |
|---|---|---|---|---|
| w | 0.0988 | $\alpha$ | 002 | 0.0988 |
| w | 0.1185 | $\alpha$ | | |
| w | 0.1289 | $\alpha$ | 111 | 0.1284 |
| w | 0.1860 | $\alpha$ | | |
| w | 0.2129 | $\alpha$ | | |
| m | 0.2195 | $\alpha$ | | |
| m | 0.2369 | $\alpha$ | 202 | 0.2371 |
| m | 0.2492 | $\beta$ | | |
| v. w | 0.2566 | $\beta$ | 300 | 0.2579 |
| w | 0.2632 | $\beta$ | | |
| m | 0.2707 | $\beta$ | 113 | 0.2705 |
| m | 0.2796 | $\alpha$ | | |
| St | 0.3018 | $\alpha$ | | |
| w | 0.3106 | $\alpha$ | 300 | 0.3111 |
| St | 0.3193 | $\alpha$ | | |
| St | 0.3259—0.3302 | $\alpha$ | 113 | 0.3261 |
| m | 0.3391 | $\alpha$ | 212 | 0.3408 |
| m | 0.4115 | $\alpha$ | 302 | 0.4099 |
| w | 0.4302 | $\alpha$ | 104 | 0.4299 |
| St | 0.6365 | $\alpha_1$ | 214, 223 | 0.6373, 0.6372 |
| w | 0.6394 | $\alpha_2$ | 214, 223 | 0.6396, 0.6394 |
| m | 0.6933 | $\alpha$ | | |
| v. w | 0.7232 | $\alpha$ | 115 | 0.7215 |
| m | 0.7464 | $\alpha$ | | |
| m | 0.7572 | $\alpha$ | 205, 322 | 0.7560, 0.7556 |
| m | 0.7744 | $\beta$ | 330 | 0.7738 |
| w | 0.7867 | $\beta$ | 404 | 0.7864 |
| w | 0.8241 | $\alpha$ | 412 | 0.8248 |
| w | 0.8454 | $\alpha$ | 314 | 0.8448 |
| v. w | 0.8912 | $\alpha$ | 501, 006 | 0.8921, 0.8919 |
| St | 0.9133 | $\alpha_1$ | | |
| w | 0.9158 | $\alpha_2$ | | |
| w | 0.9340 | $\alpha$ | 330 | 0.9334 |
| St | 0.9436 | $\alpha_1$ | | |
| w | 0.9456 | $\alpha_2$ | | |
| St | 0.9488 | $\alpha_1$ | 404, 413 | 0.9485, 0.9484 |
| w | 0.9514 | $\alpha_2$ | 404, 413 | 0.9518, 0.9517 |

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## SINOMENINE AND DISINOMENINE. XIX. ON REDUCTION OF SINOMENINE AND DIHYDROSINOMENINE WITH Na-AMALGAM.

By **Kakuji GOTO** and **Shingo MITSUI.**

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In the 11th report of this study,[1] one of the authors (K.G.), reported that he obtained by the reduction with Na-amalgam bis-[8, 8′]-demethoxy-dihydrosinomenine [VII] from sinomenine and demethoxy-dihydrosinomenine (III; d-dihydrothebainone of Speyer) from dihydrosinomenine and by Clemmensen's method demethoxy-desoxo-dihydrosinomenine (VIII; d-$\beta$-tetrahydrodesoxy-codeine) from the both starting alkaloids. Recently, Ochiai and Hakozaki[2] repeated this reduction in several different ways and could this time obtain the demethoxy-dihydrosinomeninol [VI] in well crystallised form, melting at 138°. Thus they could endorse their former view,[3] that the ketonic group of sinomenine could be reduced to the alcohol group by Na-amalgam.

Since in my first report on this problem, no mention was given in the latter point, I felt somewhat responsible to look for the alleged alcoholic base in the reduction products, and was fortunately enough to affirm the result, obtained by Kondo, Ochiai and Hakozaki.

As is shown in details in the experimental part, the chief product of the reduction of dihydrosinomenine with Na-amalgam corresponding to 4H, is the mixed crystals (m.p. 149°) of demethylated ketonic and alcoholic

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(1) This Bulletin, **4** (1929), 244.
(2) *J. Pharm. Soc. Japan*, (1930), 53–59.
(3) Ibid., (1926), 99–104.

bases. They are well defined, uniformly appearing crystalls, but could not be resolved into the components by repeated recrystallisation from organic solvents, or by repeated dissolving in alkali and precipitating with carbonic acid gas. About one half of the mixed crystalls could be transformed into the semicarbazone, and also into the iodomethylate of the demethoxy-dihydrosinomenine. Yet, the separation, as free bases, was perfectly impossible. Such cases are often met with as in aconitines, studied by Majima and co-workers[1] and in disinomenine and ψ-disinomenine of one of the authors.[2]

It is, therefore, better to reduce again these mixed crystalls with Na-amalgam in order to obtain demethoxy-dihydrosinomeninol in a pure state. When the mixed crystalls were treated with Na-amalgam corresponding to 3H or 6H in water, tne alcoholic base was obtained in beautiful four-sided rhombic crystalls from acetone. It sintered at 138°, melted at 142°, and decomposed at 143°. It formed no semicarbazone. Its rotatory power was $[d]_D^{30}=+46.8°$ and its iodomethylate decomposed at 280°. These properties well coincide with the description of Speyer and Siebert given to the dihydro-thebainone, of which our alcoholic base is regarded to be the optical antipode. The racemization was; however, not tried in this case, since Kondo and Ochiai reported four years ago that they could racemise successfully their iodomethlates.

The reason, why I did not obtain the above mentioned mixed crystalls in the former study seems entirely due to the condition of Na-amalgam used at that time. Now, it was clearly settled that the best condition to obtain the demethoxy-dihydrosinomenine [III] in a pure state is to use the fresh Na-amalgam in an amount corresponding to 3H. Less than that, the demethylated ketonic base is contaminated by much unchanged dihydro-sinomenine, whose separation presents always some difficulties.

In the course of this study, we could isolate a new alcoholic base (m.p. 162°) from that part of the reduction products of dihydrosinomenine, which is more soluble in the sodium carbonate solution containg much $CO_2$. The new alcoholic base has the formula $C_{19}H_{27}NO_4$, is monomolecular, retains two methoxyls and does not form semicarbazone. Its properties are given in the second column of the Table 1. The yield was 1/5~1/10 of the above mentioned demethylated bases.

The formation of this new alcoholic base is quite intelligible from the constitutional formula of sinomenine [I] proposed by one of the authors (K.G.). According to it, sinomenine is an $\alpha$, $\beta$-unsaturated ketonic base,

(1) Majima and Morio, *Ann.*, **476** (1929), 194.
(2) Goto, this Bulletin, **4** (1929), 129.

having an enol-methylether in the $\alpha$-position. And the easy reduction of the methoxyl group by Na-amalgam is undoubtedly caused by the loosening (auflockende) action of the vicinal ketonic group. Now, in the course of the reduction, those molecules of dihydrosinomenine, whose ketonic group was first attacked and transformed into the alcohol, will loose this action on the methoxyl group, so that the methoxyl on $C_{(7)}$ may be kept intact to the last. The new alcohol base will be called, therefore, dihydro-sinomeninol.

Table 1.

| | Demethoxy-dihydro-sinomeninol (VI) | Dihydrosinomeninol (V) | Sinomeninol (IV) |
|---|---|---|---|
| Yield | 12–30% | > 50% | > 30% |
| Mol. formula | $C_{18}H_{23}NO_3$ | $C_{19}H_{27}NO_4$ | $C_{19}H_{25}NO_4$ |
| Solvents for recrystallisation | Acetone or ethyl acetate | Metyl alc. or benzene | Mehtyl alc., but not benzene |
| M.p. | 138° (sinters) 143° (dec.) | 160° (sinters) 162° (dec.) | 125° (sinter) 127° (dec.) |
| $[\alpha]_D$ | +46.8° | +1.93° | −23.7° |
| No. of Methoxyls | 1 | 2 | 2 |
| Formation of semicarbazone | No | No | No |
| M. p. of iodomethylate | 280° (dec.) | 249° (dec.) | 272° (dec.) |
| $FeCl_3$-reaction | Green | Green | Green |
| Diazo-reaction | 2,000,000* | 2,000,000 | 2,000,000 |
| $FeK_3(CN)_6$-reaction | 500,000 | 500,000 | 500,000 |
| Formaline-sulphuric acid reaction | Yellow → green → violet | Yellow → green → blue | Yellow → green → blue |

* The figures show the dilution, at which the colour of the reactions is still visible.

The ratio of the reduction velocity of the ketone and the methoxyl groups in hydro-sinomenine may be calculated as about 10:1, on the basis of the yield of demethylated ketonic base and that of dihydro-sinomeninol. It is, therefore, very difficult to obtain the new base in a better yield by the alkaline reduction. We tried, accordingly, to reduce the ketonic group in acidic medium by Na-amalgam. As was seen in the catalytic reduction and in the Zn-amalgam reduction in the cold, sinomenine retains mostly its methoxyl group and the yield of hydrosinomenine amounts to the quantitative in the former case, and more than 50% in the latter. If we carry out

the reduction of hydrosinomenine quickly in an acidic medium, the yield of dihydrosinomeninol may be increased.

This is actually so. In reducing hydrosinomenine in a dilute acetic acid solution with Na-amalgam corresponding to 6 H (considering the enormous loss of hydrogen) in half an hour, the yield of dihydrosinomeninol amounted to more than 50%. It melted at 162°, without depression even when admixed with that obtained in an alkaline reduction. All the other properties of both substances, originated from these two sources, coincided perfectly.

If the above supposition regarding to the formation of dihydrosinomeninol is correct, then sinomenine itself might be reduced to sinomeninol [IV], without loosing its double linking as well as its enol-ether group. This is also actually the case. When sinomenine hydrochloride was reduced quickly in a dilute acetic acid solution as above described, a new base (m.p. 127°) was obtained in a yield about 30%. Its elemental analysis corresponds to $C_{19}H_{25}NO_4$ (thus isomeric with dihydrosinomenine), it has two methoxyls, is monomolecular and does not form semicarbazone. The other properties are given in the third column of the Table 1.

The most striking properties of the sinomeninol are two. First, it is laevorotatory as sinomenine itself is. When the double linking of sinomenine was transformed into the single linking, the base invariably changes its direction of the rotation, no matter how this transformation was effected. Thus, sinomenine hydrate is dextrorotatory as dihydrosinomenine is. This unchanged direction of the rotation of sinomeninol speaks most fluently for the fact that the double linking of sinomenine was not attacked in the above reduction. But the decisive proof was given by the fact that sinomeninol could be reduced into dihydro-sinomeninol (m.p. 162°) by Pd + $H_2$. For, it is a known fact that the double linking of the phenanthrene alkaloid can be reduced catalytically,[1] whilst the reduction of a ketonic group goes on with much difficulty.[2]

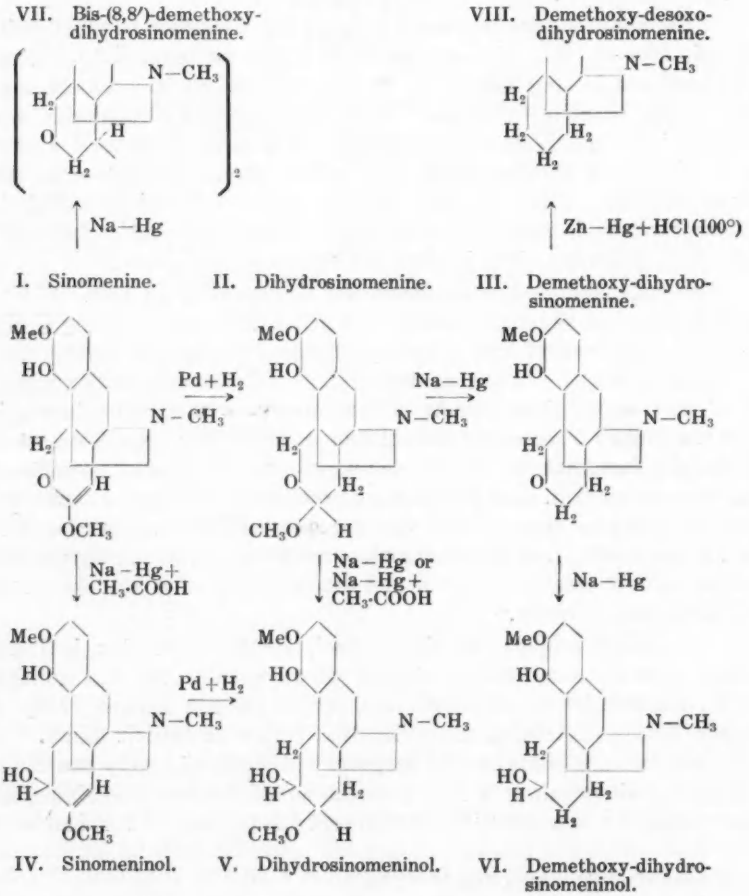
The second property of sinomeninol, worthy of mention, is that it dissolves in caustic alkali without taking yellow colour. As was noticed first by R. Robinson,[3] those substances, which have a ketone group and a double linking in conjugation, dissolves yellow in caustic alkali. In this point, sinomenine partakes the property of thebainone, only the difference being that sinomenine does not give the halochromy of thebainone against conc. mineral acids. This shows also that the position of the double linking

(1) Freund, *J. prakt. Chem.*, **101** (1921), 12.
(2) Skita, *Ber.*, **54** (1921), 1562.
(3) Gulland and Robinson, *J. Chem. Soc.*, **123** (1923), 996.

may be reversed in thebainone and sinomenine. In this point, the recently proposed formula of thebainone by C. Schöpf[1] explains the property of thebainone as well as of sinomenine in some sense. Anyhow, the formation of sinomeninol and dihydro-sinomeninol gives one more proof that sinomenine must be an $\alpha$, $\beta$-unsaturated, $\alpha$-enolic ketone.

The relation of the bases, obtained hitherto by the reduction of sinomenine and dihydrosinomenine are given in the following Table 2.

Table 2.




(1) Schöpf, *Ann.*, **468** (1927), 158.

**Conclusions.** 1.—The best condition to obtain demethoxy-dihydrosinomenine (III) from dihydrosinomenine is to reduce the latter with Na-amalgam corresponding to 3H.

2.—In using Na-amalgam corresponding to 4H in the above reduction, the chief product is the mixed crystalls of the demethylated ketonic and alcoholic bases (III+IV). As an accessory product, dihydrosinomeninol (V) is obtained.

3.—To prepare the demethoxy-dihydrosinomeninol in a pure state, it is better to reduce again the above mixed bases with much Na-amalgam.

4.—Dihydrosinomeninol is also produced by the Na-amalgam reduction of dihydrosinomenine in an acetic acid solution. The phenols C and D of Ochiai and Hakozaki, which they think to be two new isomerides of the demethoxy-dihydrosinomenine, are probably one and the same substance and are nothing but our dihydrosinomeninol.

5.—By reducing sinomenine in an acetic acid solution sinomeninol (IV) is produced. This is identical with the phenol F of Ochiai and Hakozaki. But they assigned to this base the dimeric formula $(C_{18}H_{24}NO_3)_2 \cdot H_2O$ and assumes it to be consisted of two molecules of an isomeric (?) demethoxy-dihydrosinomeninol.

## Experimental.

**Note on the Preparation of Dihydrosinomenine.** Dihydrosinomenine can be prepared very easily from sinomenine by means of catalytic reduction with palladinised charcoal and hydrogen. The mixture, consisting of sinomenine hydrochloride (50 gr.) in 400 c.c. hot water, 0.3 gr. $PdCl_2$ in 40 c.c. dil. hydrochloric acid and charcoal (5 gr.), was shaken, while hot, vigorously with hand in a hydrogen atmosphere. The sorption of hydrogen amounts to 3600 c.c. (somewhat more than one molecule) in 15~30 minutes. Yield almost quantitative. M.p. 198° (from methyl alcohol).

The careful treatment of the methyl alcoholic mother liquor did not give other base than dihydrosinomenine.

Anal. Found: C=68.54; H=8.02; N=4.55. $C_{19}H_{25}NO_4$ requires: C=68.84; H=7.6; N=4.23%.

Sp. rotatory power, measured in chloroform: $[\alpha]_D^{25}=+193.58°$; measured in dilute hydrochloric acid: $[\alpha]_D^{24}=+33.06°$.

Oxim: m.p. 211° (dec.).

Semicarbazone: m.p. 209° (dec.) (Found: N=14.69%. Calculated for $C_{20}H_{28}O_5N_4$: N=14.43%.

Iodomethylate: m.p. 268° (dec.); solubility in water 0.34% (at room temperature).

*Reduction of hydrosinomenine with Na-amalgam (corresponding to 4H).*- Hydrosinomenine (8 gr.) is suspended in 2% NaOH (80 c.c.) and is added with 5% Na-amalgam (50 gr.) After 24 hours, the aqueous part is diluted with water (80 c.c.) and supersaturated with $CO_2$. The pasty precipitate, first formed, changes gradually into rhombus plates, which are collected. The filtrate contains dihydrosinomeninol [IV].

The rhombus plates are again dissolved in 4% NaOH and precipitated with $CO_2$. This treatment is repeated once again. The united filtrate contains sometimes demethoxy-dihydrosinomenine [III].

The rhombus plates are finally recrystallised from acetone. When the substance crystallise out slowly, it forms stout prisms, but showing different faces more or less developed. M.p. 144° (dec. at 149°). These are the mixed crystalls of demethylated ketonic and alcoholic bases [III+VI], and can not be easily resolved by recrystallisation.

From 1 gr. each of these crystalls, 0.3 gr. and 0.4 gr. of semicarbazone was obtained.

From 1 gr. of these crystalls, 0.5 gr. of demethoxy-dehydrosinomenine iodomethylate (m.p. 120°) is obtainable. The rest of the iodomethylate, which is more soluble in water, melts at 278°.

From these results, the mixed crystalls must be consisted of almost equall parts of the two bases.

Methoxyls. Found: 10.68% (calc. for one: 10.23%)

**Demethoxy-dihydrosinomeninol (VI).** The above mentioned mixed crystalls are again reduced with 5% Na-amalgam, corresponding to 8H. The precipitate formed by $CO_2$ is not rhombus plates this time, but remaines pasty. This precipitate is purified through chloroform and recrystallised from acetone. It forms then nice rhombus plates, which softens at 138°, melts at 142° and decomposes at 143°. Yield about 50% (about 12.5% of dihydrosinomenine).

For the properties, see the first column of the Table 1.

Sp. rotatory power: 0.419 gr. subst. was dissolved into 10 c.c. methyl-alcohol. $\alpha = +0.98$; $d = 0.5$ dm. Therefore,

$$[\alpha]_D^{20} = (0.98 \div 0.419) \times (10 \div 0.5) = +46.8°$$

It does not form semicarbazone; the starting material was recovered almost quantitatively in this trial.

Iodomethylate; long prisms from methyl alcohol. M.p. 280°. Very soluble in water, but recrystallisable from it.

**Dihydrosinomeninol (V).** (A) This base was isolated from sodium carbonate solution, from which the precipitate of the above described mixed bases was removed. Twice recrystallised from methyl alcohol, it forms nice

prisms and melts at 162° sharply, softening at 160°. Yield 4% and 6% each in two isolations.

(B) Hydrosinomenine (9.5 gr.) was dissolved in 6% acetic acid (50 c.c.) and added with 5% Na-amalgam (corresponding to 6H) in five portions, accompanied by the addition of glacial acetic acid to keep the solution always acidic (20 c.c. in total). The reduction finishes in 30 minutes. The base is isolated in the ordinary way, and recrystallised from methyl alcohol (60 c.c.). Yield 5 gr. (over 50% of the theoretical). M.p. 162°. The admixed m.p. with the preparate obtained in (A) shows no depression.

For the properties, see the second column of the Table 2.

Anal. Found: C=68.16; H=7.81; N=4.18; methoxyls=18.74%. $C_{19}H_{27}NO_4=333$ requires: C=68.46; H=8.11; N=4.21; methoxyls (2)=18.62%. The analysed substance was dried at 120°~130°.

Sp. rotatory power, measured in methyl alcohol: (A) the substance obtained by alkaline reduction.

$$[\alpha]_D^{20} = (0.07 \div 0.453) \times (25 \div 2) = +1.93°.$$

(B) the substance obtained by acidic reduction.

$$[\alpha]_D^{20} = (0.07 \div 0.499) \times (25 \div 2) = +1.75°$$

Mol. Weight, measured after Rast: $(179 \div 1525) \times (400 \div 16.15) \times 100 = 291$.

The substance does not give semicarbazone, but the starting substance was recovered in a good yield in this trial.

Iodomethylate: Both the iodomethylates from the sources (A) and (B) can be obtained by mixing the bases with methyliodide in methyl alcohol. They crystallise out in tetragonal or octagonal oblong plates, when the methyl alcohol is evaporated off. Recrystallised from water, it sinters at 218°, become waxy at 244° and decompose at 249°. (Found: J=26.88% Calc.: J=26.74%).

The spe ific rotatory power of the both iodomethylates are almost equal, when measured in aqueous solutions.

$$[\alpha]_D^{28} = -(0.35 \div 0.557) \times (10 \div 1) = -6.28 \quad \text{(from the source A)}$$

$$[\alpha]_D^{28} = -(0.40 \div 0.594) \times (10 \div 1) = -6.73 \quad \text{(from the source B)}$$

It is interesting to note, that both the iodomethylates are laevorotatory, in opposition to their free bases. Such inversion is often met with in amino-acids and in some of the alkaloids with carboxyl group.

In any way, the identity of the dihydrosinomeninols obtained by alkaline and acidic reductions seems to have been settled beyond doubt.

**Sinomeninol** (IV). 5% Na-amalgam (250 gr. corresponding to 10H) was put in a stout Erlenmeyer's flask, poured on with 100 c.c. of 20% sinomenine hydrochloride solution and added with glacial acetic acid in portions (50 c.c. in total), whilst the solution was cooled with ice-water from time to time. The reduction ends in 15 minutes. The isolated base is recrystallised twice from methyl alcohol. M. p. 127° (softening at 125°). Yield 5 gr. (over 30%).

For the properties, see the third column of the Table 1.

Anal. Found: C = 68.39, 68.73; H = 7.83, 7.81; N = 4.23; methoxyls = 18.59%. $C_{19}H_{25}NO_4$=331 requires: C=68.88; H=7.56; N=4.23; methoxyls (2)=18.73%.

Mol. weight, measured after Rast: $(150 \div 1632) \times (400 \div 11.6) \times 100 = 328$.

Sp. rotatory power, measured in chloroform: $[\alpha]_D^{28} = -(0.92 \div 0.39) \times (10 \div 1) = -23.7°$

The base does not give semicarbazone, but the starting material is recovered in a good yield.

Iodomethylate: prepared in the methyl alcohol. Teragonal, oblong plates from methyl alcohol, but recrystallisable from water into long prisms. M.p. then 272° (dec.) (Found: I=26.88%. Calc.: I=26.74%).

**Catalytic Reduction of Sinomeninol.** Sinomeninol (1 gr.) was dissolved in dilute hydrochloric acid (110 c.c.), added with $PdCl_2$ (0.05 gr.) and charcoal (1 gr.) and shaken, while warm, in a hydrogen atmosphere. The sorption of hydrogen amounts to 97 c.c. (more than 2 H) in 40 minutes. The base, isolated in the ordinary way recrystallised from benzene, melted at 162°. Yield good. The admixture with the dihydrosinomeninol, obtained from dihydrosinomenine, does not lower the melting point.

**Note.** The constitution of sinactine (*l*-tetrahydro-epi-berberine[1]) is to be regarded the 18th report of this study.

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(1) *J. Chem. Soc.*, (1930), 1234.